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# Catalyst design for enhanced sustainability through fundamental surface chemistry

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# Summary

Decreasing energy consumption in the production of platform chemicals is necessary to improve the sustainability of the chemical industry, which is the largest consumer of delivered energy. The majority of industrial chemical transformations rely on catalysts, and therefore designing new materials that catalyse the production of important chemicals via more selective and energy-efficient processes is a promising pathway to reducing energy use by chemical industry. Developing new catalysts requires an integrated approach involving fundamental experimental studies and theoretical modelling in addition to evaluation of materials under working catalytic conditions. In this review, we outline this approach in the context of a particular catalyst—nanoporous Au (npAu)—which is an unsupported, dilute AgAu alloy catalyst that is highly active for the selective oxidative transformation of alcohols. Fundamental surface science studies on Au and AgAu alloy single crystals identified three principles which define the reactivity of npAu and enable prediction of new reactive pathways on this material: (1) oxygen adatoms are necessary for reaction, (2) silver plays an important role in supplying oxygen atoms by dissociating molecular oxygen, and (3) weak binding interactions are key to the selectivity of npAu. We also briefly describe other systems in which this integrated approach was applied.

# Main Text

### 1. Introduction

For global energy security, there is an absolute imperative for a transformational approach to downsizing the energy footprint of the chemical industry. Chemical industries are the second largest users of energy in the manufacturing sector and the largest for delivered energy (19 percent of total global energy use in 2010) [1]. Current worldwide energy demand and consumption will increase from 524 quadrillion Btu in 2010 to 820 quadrillion in 2040, an increase of 56 percent. This fact alone supports the need for new, innovative, sustainable catalytic conversion processes to offset this global consumption within the industrial market. Given that the industrial sector, including the manufacturing of bulk chemicals, uses more delivered energy than any other end-use sector, the need for new and sustainable catalytic processes is all the more urgent. In the United States, the industrial sector is responsible for nearly a third of total energy use, where consumption is in energy-intensive processing. Breakthroughs are required so that bulk manufacturing of chemicals is performed at lower temperatures and catalytic conversion reactions are more selective and energy efficient.

An interdisciplinary approach, including both experiment and theory, is required to obtain fundamental understanding of catalyst reactivity for the purpose of developing catalytic processes that have

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high conversion and high selectivity, thus, increasing their sustainability. Understanding reaction selectivity under catalytic conditions will (1) lead to new opportunities to decrease fuel consumption, and (2) create more efficient and selective processes with benign by-products. This understanding will also advance some of the most important scientific challenges, including the design of atom- and energy-efficient syntheses of revolutionary new forms of matter with tailored properties. Through the direct and controlled assembly of novel nanoscale and mesoscale structures, new functionalities of advanced heterogeneous catalytic systems are possible, providing opportunities for more efficient, benign, durable, and/or 'sustainable' catalytic systems.

Future energy needs call for dramatic increases in the *sustainability* of chemical production. Meeting this challenge requires deep insight into how to control reaction selectivity for networks of complex transformations. It also relies on innovative design of *new types* of catalytic materials. Accordingly, one avenue of current work in catalysis focuses on developing a *predictive* mechanistic framework for controlling reaction selectivity and activity on new mesoporous catalytic materials designed to optimize activity and selectivity for specific reactions important for sustainable chemistry. Materials and their functions are examined under highly controlled conditions afforded by low-pressure surface science methods and also under working catalytic conditions of pressure and temperature. This approach allows the development of a general framework to predict activity and reactivity for selective reactions on different length, time and (reactant) density scales. Correlating advanced imaging techniques and *in situ* spectroscopies with studies of reactivity under model and reactor conditions provides key information for relating reactivity to geometric and electronic structure, critically linking with theoretical work for guidance and refinement. One goal of a particular branch of research utilizing this approach is to develop a revolutionary new generation of catalysts based on a thorough understanding of novel non-zeolitic nanoporous, mesoscale forms of matter with tailored catalytic properties, up-scaling from molecular-scale understanding to catalytic operating conditions.

Meso- and nanoporous nonzeolitic materials [2] are complex structures with a large fraction of the atoms on the surface, many of which are in low coordination sites (i.e., few near neighbours). These materials are highly crystalline, mechanically strong [3,4] and thermally robust. The promise of novel functionality that may arise from assembling matter into mesoscale structures is a prime motivation for studying these materials. Broader investigation of these porous frameworks as catalysts for selective chemical transformations is motivated by studies, by our research group and others, of selective oxidation processes catalysed by nanoporous gold [5-7]. Nanoporous gold (npAu), as commonly prepared, is a dilute AgAu alloy containing 1-3% Ag and serves as a catalyst without the need for a support [2,8]. It is effective for selective oxidation processes at low (near ambient) temperature over ten orders of magnitude in gas pressure, and even in solution [5-7,9-13]. Subsequent to this ground-breaking discovery, other nanoporous metals are starting to be explored for catalytic activity; for example, npAg has recently been used as a catalyst for selective oxidation of alcohols [14]. Moreover, a few recent studies of CO oxidation on npAu stabilized with metal oxide overlayers demonstrate their improved thermal stability [15,16]. Most recently, np$TiO_2$ catalysts doped with small amounts of Au for cycloaddition [17] reactions demonstrated the promise of generalizing these architectures to metal oxides.

In this overview, we demonstrate how the study of the partial oxidation of alcohols catalysed by npAu illustrates the efficacy of nanoporous materials for selective catalysis as well as our ability to bridge vastly different regimes of materials complexity and reaction conditions in order to construct a comprehensive model for catalytic activity. For example, methanol coupling to methyl formate is selectively catalysed on npAu at atmospheric pressure [6] via the mechanism determined from fundamental, model studies on an O-covered Au(111) single crystal [18]. Similar results are observed for npAu in surface science experiments under low pressure conditions [9]. More generally, the mechanism for coupling of dissimilar alcohols obtained from surface science experiments [19] applies to catalytic conditions. These selected examples show that mechanisms derived from fundamental experimental studies, in combination with theory, map directly onto reactions at atmospheric pressure.

These mechanisms are then used to build general models that predict patterns of reactivity for analogous reactants and to establish salient factors that control reactivity and selectivity, both under low pressure and catalytic conditions, thereby guiding the development of more sustainable catalytic systems. Specifically, three key principles determined from low-pressure model studies define the reactivity of complex npAu alloy catalysts at atmospheric pressure. First, oxygen atoms are necessary for reaction on Au and on Ag.

Second, Ag plays a key role in supplying this oxygen to npAu by dissociating molecular oxygen. Finally, rapid diffusion of reactants on Au due to weak bonding interactions is key to the selectivity of the npAu catalyst system. Defining catalytic principles in this way enables the design and optimization of catalyst materials and reactant conditions to establish sustainable and energy-efficient catalytic systems.

## 2. Correlating Across Pressures and Compositions: The Role of Oxygen and Oxygen Dissociation

An excellent example of the applicability of model studies in predicting and understanding the reactive behaviour of complex materials is the deceptively simple first step in activating these catalytic materials for oxidative chemistry: the dissociation of dioxygen to form adsorbed oxygen atoms. Both the identification of dioxygen dissociation as a key prerequisite for oxidative transformations on gold, silver, and their alloys, and the understanding of the mechanism by which this process takes place originate with model studies on single crystals under well-controlled low pressure conditions [20-22]. Specifically, Au(111) and Ag(111) have been used as model surfaces for many of these surface science studies because the (111) surface is the facet most commonly exposed by supported nanoparticles (and unsupported nanoporous Au) due to the thermodynamic stability of the hexagonally close-packed structure of the (111) plane [23]. Mixed Ag/Au alloys prepared via the evaporation of Ag onto Au single crystals have also been studied and their reactive properties compared in detail to pure Ag and Au surfaces, in order to elucidate the roles of Au, Ag, and mixed sites in the binding and chemical transformation of adsorbed species. Subsequent mapping of the reactivity of these single crystal materials under well-controlled, low pressure conditions onto the reactivity of complex materials under ambient pressure is possible due to the relative inertness of Au. Because of this inertness, at ambient pressure conditions there is a relatively low steady-state coverage of oxygen, reactive intermediates, and spectator species such as water, thus reflecting the state of the metal surface under low-pressure conditions [22].

The clean Au(111) surface is ***not*** active for the dissociation of dioxygen [21]. However, a number of methods yield adsorbed atomic oxygen on the Au(111) surface by increasing the chemical potential for oxidation. Notably, at least two of these methods—electron bombardment of adsorbed $NO_2$ and dosing ozone—result in restructuring of the Au surface [20,24,25]. In the case of the $NO_2$ method, the herringbone reconstruction of Au(111) reversibly rearranges to form Au islands which are visible with scanning tunnelling microscopy (STM) [20]. With ozone deposition, Au atoms are released from the surface to form nanoparticles containing both Au and O [22]. In both instances, the rearrangement of the Au surface and the release of Au atoms to form nanostructures facilitate the dissociation of $O_2$ although it does not lead an overall increase in the concentration of adsorbed O [20,22]. Further, the rearrangement influences the binding site of the O atoms on the surface, thus affecting reactivity [22].

Three different types of O bound to Au have been identified using vibrational spectroscopy, and their relative abundance on the surface changes with O coverage and temperature [22]. Oxygen atoms can chemisorb onto the surface of Au, they can be incorporated in a surface oxide which also contains Au atoms, or they can be part of a subsurface oxide. These different forms of oxygen result in different reactivity and selectivity. Specifically, oxygen chemisorbed on the surface is highly active for oxidative transformations of alcohols and olefins, as well as for CO oxidation. This binding site is favoured at low O concentrations—the conditions at which are selectivity and activity are optimal on Au for these same reactions. Theoretical studies have shown that, at low coverage, O prefers 3-fold sites on Au(111), Au(321), the reconstructed Au(110) surface, and the reconstructed Au(100) surface [26,27], although on the Au(211) surface a 2-fold coordinated site is preferred [28]. While O chemisorption is strengthened by roughening of the Au(111) surface, isolated O atoms do not bind directly to Au adatoms or sit in vacancies. Instead, the atoms bound at 3-fold sites are stabilized by the presence of neighbouring vacancies resulting from this rearrangement [21,22]. A number of stable O-Au surface oxide structures have been identified on Au(111) using density functional theory (DFT), and these structures are predicted to be the most thermodynamically stable under a variety of conditions, including temperatures and $O_2$ pressures for typical catalytic reaction conditions [26]. Subsurface O has also been observed on Au(111) during molecular dynamics calculations, but only occurs at a coverage greater than 0.33 ML [29].

This understanding of O binding to Au(111) surfaces is key in deconvoluting the multiple O recombination features observed during desorption experiments involving AgAu single crystal alloys [30].

These single crystal alloy studies in turn provide a bridge to understanding $O_2$ dissociation on AgAu alloy materials with a greater degree of structural complexity, such as npAu, under well-controlled low pressure conditions [31]. The recombination of O atoms to form molecular oxygen is the microscopic reverse of $O_2$ dissociation, and the peak temperatures for O recombination are diagnostic of the different $O_2$ dissociation sites on the crystal surface [21].

Two recombination peaks are observed for O on the AgAu(111) thin-film alloy surface: Au-like sites, indicated by a peak for $O_2$ recombination with a temperature similar to that on Au(111) (525K), and mixed sites, identified by a $O_2$ recombination peak whose temperature (540K) falls in between that of Au(111) and Ag(111) [30]. Notably, no peak is observed for Ag-like $O_2$ recombination (595K). The recombination of O on the Au-like or mixed sites is influenced by both the O coverage and the Ag content of the alloy, with desorption from mixed sites dominating at low O coverages and high Ag content. Analogously, on npAu in low-pressure surface science experiments, O recombination occurs at 550K, which is comparable to the mixed sites on the AgAu single crystal alloys and suggests that despite differing materials complexity, the mechanism of $O_2$ dissociation on the two AgAu alloy materials is similar [31].

In contrast to single-crystal Au, nanoporous $Ag_{0.03}Au_{0.97}$ is capable of dissociating $O_2$ albeit only after of cleaning using ozone [9]. This ozone treatment removes adventitious bulk carbon from the surface of the inactive as-prepared npAu. There may also be changes in the composition and structure of the np $Ag_{0.03}Au_{0.97}$, currently under investigation in our laboratory. The ratio of $O_2$:$CO_2$ evolution resulting from ozone treatment was used to monitor the progress of the cleaning process. A similar ozone treatment is also required to reproducibly activate npAu for reaction under atmospheric pressure catalytic conditions, and this process which will be discussed in detail in a later section [32].

Theoretical work modelling $O_2$ dissociation on npAu has focused on rough Au surfaces with various amounts of Ag. Strikingly, surfaces with small ensembles of Ag generally have similar adsorption energies and dissociation barriers to the pure Au surfaces [33,34]. This suggests that the sites that are active for $O_2$ dissociation either have high local concentrations of silver, are of a very specific form, or both. Ozone activation may help enrich the surface with Ag and allow these sites to form.

In addition to understanding the mechanism of $O_2$ dissociation, determining the identity of the active oxygen species (atomic or molecular oxygen) on npAu is of key importance in understanding and predicting the reactivity of npAu under both low pressure and catalytic conditions. Through judicious control of the oxygen dosing temperature in surface science studies on npAu, atomic O was identified as the oxygen species which is responsible for the oxidative reactivity of npAu [31]. Intact molecular oxygen desorbs from npAu below 300K under well-controlled low-pressure conditions and therefore dosing $O_2$ at 300K leaves only adsorbed atomic O on the surface. *Only* atomic O bound to np $Ag_{0.03}Au_{0.97}$ leads to selective oxidative coupling of alcohols, such as methanol, to form esters, such as methyl formate [31]. These investigations demonstrate that atomic $O_{ads}$ is required for reactions with alcohols. Although theoretical studies suggest that $O_2$ may play a direct role in CO oxidation [35], there is no experimental proof of such a mechanism.

## 3. Predicting Reactivity from Fundamental Studies: Oxidative Self-Coupling of Methanol

From the above studies of oxygen activation on single crystals and $npAg_{0.03}Au_{0.97}$, it can be concluded that the same active species—atomic O—is present on each of the materials. For Au(111), active O is directly dosed to the surface [20,22,24], while for $npAg_{0.03}Au_{0.97}$, molecular oxygen is dissociated with the assistance of Ag to form adsorbed active O [30,31]. Due to this correspondence between materials, knowledge of the reactivity of Au and AgAu alloy single crystals with adsorbed oxygen can be used to actively *predict* reactivity on npAu. For example, the observation that O/Au(111) and O/AgAu promote coupling of methanol to form the ester, methyl formate [18,36], led to the correct prediction that npAu would catalyse the same reaction. Indeed, not only does npAu catalyse this selective oxidative transformation in the presence of oxygen under low pressure conditions [9], it also does so with high selectivity (100%) at atmospheric pressure in the absence of a support material [6,32]. Under either set of conditions, the reaction on npAu follows the mechanism determined from model studies on single crystals, beginning with activation of the methanol O-H to form adsorbed methoxy [6,18,36,37].

The primary functional group of alcohols is the hydroxyl group, which has a greater Brønsted acidity than water, and which is responsible for the reactivity between alcohols, such as methanol, and the O-covered Au surface. This acidity enables activation of the alcohol O-H by adsorbed oxygen, thereby forming adsorbed alkoxy and water [18,37]. The presence of methoxy on the O/Au(111) surface has been confirmed by vibrational spectroscopy and isotopic labelling [18]. Formation of adsorbed methoxy is then followed by cleavage of the C-H bond on the methyl group to generate adsorbed formaldehyde [18,37]. The eliminated hydrogen atom, bound to an atom (carbon) which is β to the Au surface (two atoms away) is referred to in what follows as the "β-hydrogen" and this C-H cleavage is called "β-hydrogen elimination" [37]. Formaldehyde is weakly bound to the surface, allowing it to migrate and be attacked by an adsorbed methoxy to yield the coupling product, methyl formate [18,37]. Some formaldehyde also reacts further to form formic acid, $CO_2$, and water or desorbs intact. The selectivity to methyl formate is highest at low O coverages, while high O coverages lead to complete combustion to $CO_2$ and $H_2O$, with no production of methyl formate [18].

Theoretical studies have also shown that the presence of O or OH can dramatically decrease activation barriers for the steps in oxidative self-coupling of alcohols on Au [36,38,39]. For example, transfer of H to O instead of directly to the surface reduces the activation energy for O-H bond cleavage from 152 to 39 kJ/mol, and it reduces the activation energy for methoxy's β-hydrogen elimination from 62 to 47 kJ/mol. In the vapour phase, adsorbed O, OH or $CH_3O$ all reduce the activation energy for β-hydrogen elimination, which is the step with the highest barrier for activation of the alcohol. The subsequent steps, coupling of methoxy and formaldehyde and another β-hydrogen elimination step, are essentially barrierless, which may explain the high selectivity to methyl formate observed experimentally. In aqueous conditions, the concentration of OH can be increased by operation at high pH; however, in the vapour phase, OH bound to Au(111) is unstable with respect to disproportionation resulting in an extremely low steady state coverage of OH.

The theoretical studies also provide broader insight into why Au-based materials are unique in their ability to catalyse the coupling reactions over other dehydrogenation products, e.g. formaldehyde, CO or $CO_2$. One key aspect of the coupling reaction is that the methoxy oxygen must move out of its preferred binding site in order to attack the carbonyl carbon of the aldehyde, e.g. formaldehyde. This process, therefore, requires partial metal-O bond breaking in the transition state. Accordingly, the barrier for this process should scale with metal-O bond strength. Since the Au-O bond strength is weaker than other transition metals, the barrier should be lowest for it. Secondly, the aldehyde must be in proximity to the methoxy for coupling to occur; thus, facile diffusion, as is the case on Au(111) is an important part of this process. Third, hydrogen atoms are only weakly bound on Au(111) so that C-H bond scission does not occur readily in the absence of other proton acceptors, e.g. atomic O, OH or other alkoxides. On other metals, even Ag but also Pd, C-H cleavage is more facile which brings dehydrogenation pathways into play. This broader framework provides a means of understanding transformations of methanol on metal surfaces more broadly and also for predicting and understanding the reactivity of longer-chain alcohols (see below).

On AgAu alloy crystals, the mechanism for the selective oxidative coupling of methanol is largely analogous to that on Au(111), but differs in that there are three different formation sites for methyl formate: Au-like sites, Ag-like sites, and mixed sites [30]. This is similar to the case of $O_2$ recombination on AgAu(111) tin-film alloys, and the relative amount of methyl formate produced at each type of site varies with the Ag content of the alloy. When the Ag content is relatively low ($Ag_{0.15}Au_{0.85}$), the majority of methyl formate production (75%) originates from Au-like sites, with the remainder of the methyl formate being produced on mixed sites [30]. Coupling on mixed sites increases with Ag content at the expense of reaction on Au-like sites, but only on alloys with very high Ag content ($Ag_{0.6}Au_{0.4}$) do Ag-like sites begin to contribute even a small amount of methyl formate production (< 1%). The production of hydrogen confirms that surface-assisted β-H elimination does occur on mixed sites, as H recombination to form $H_2$ occurs on Ag single crystals but not on Au [30]. The yield of methyl formate also increases with increasing Ag content, and methyl formate production on O/$Ag_{0.6}Au_{0.4}$ is 50% higher than on O/Au(111) [30].

Previous work on alcohol oxidation on AuPd may give insight into the roles of the Ag and Au in the alloy [39]. It has been shown that increased amounts of Pd decrease the activation barrier for β-hydrogen elimination from methoxy. However, larger ensembles of Pd adsorb intermediates quite strongly. Therefore, neither pure Au nor large ensembles of Pd are desirable, and the same may apply for Ag in Au.

As with Au(111), the production of methyl formate on AgAu alloys is also dependent on O coverage. At low O coverage, the selectivity to methyl formate is high [30]. Formaldehyde is also formed as a product, but there is no detectable $CO_2$ produced. In contrast, at high O coverages, reactivity is dominated by combustion. An initial increase in O leads to a corresponding increase in methyl formate production, but a continuing increase in O coverage results in the decline of methyl formate and formaldehyde production as combustion becomes the favoured process [30]. Depending on the O coverage, $CO_2$ production has been observed at sites of all three metal compositions. On npAu at low-pressure conditions, the distribution of products is 20% methyl formate, 34% formaldehyde, and 46% $CO_2$, which represents a similar distribution of species to that observed on AgAu alloys, though directly analogous Ag contents and O coverages were not studied [9]. These trends can be mapped onto atmospheric pressure conditions, where npAu materials display the same dependence on O concentration and Ag content.

Through optimisation of the npAu material and the reaction conditions, 100% selectivity to methyl formate was achieved on npAu with < 3% Ag in the catalyst material and a relatively low concentration of $O_2$ in the reactant stream under flowing conditions at atmospheric pressure [6,32]. At higher Ag contents and $O_2$ partial pressures, selectivity shifts toward combustion, with combustion being the exclusive process at >10% Ag [6]. As stated previously, the fundamental selective surface chemistry is largely the same on npAu as on the O/Au(111) surface, except that in the case of npAu the residual silver serves to dissociate molecular oxygen. In initial work with methanol coupling on npAu at atmospheric pressure, 100% selectivity to methyl formate and 10% conversion were observed for a stoichiometric ratio of methanol and $O_2$ (1% $O_2$/ 2% methanol) at temperatures as low as 293 K [6]. At higher temperatures, the conversion increases and the selectivity decreases slightly, with a 60% conversion and 97% selectivity to methyl formate at 353 °K. The competing process is combustion to produce $CO_2$—no formaldehyde or formic acid is produced under ambient pressure flow conditions [6,32]. At low temperatures (303 K), the catalyst used in this initial work was stable for over seven days [6].

The npAu catalysts used in this initial work were as-prepared npAu ingots which had been activated in flowing reactants ($O_2$ and methanol and/or CO) [6]. While this activation procedure worked in a number of published studies, we have since found it to be highly sensitive to catalyst preparation, leading to irreproducible activation of npAu catalyst materials [32]. Some npAu ingots activated, others activated and then deactivated, while still others never activated after an extended time on stream. In addition, we found that the ingots have mass transport limitations, which led us to explore other architectures of npAu, such as 100 nm thick foils and 400 nm thick hollow shells, in order to overcome these limitations [32]. Therefore, it became necessary to develop a method for reproducibly and stably activating npAu materials regardless of their sample preparation [32]. The reproducible activation of catalytic materials with sustained activity is also an important general challenge in catalysis as a field.

The method we developed for activating these materials for catalytic reaction under atmospheric conditions was based on the previous work we had done involving the activation of npAu under low pressure conditions, discussed above, by using ozone to remove adventitious carbon from the as-prepared material [9]. The activation sequence for reaction at ambient pressure involves treating npAu materials in ~ 3% ozone at 423 K followed by purging with He and cooling to room temperature and then heating to 423 K in a mixture of methanol and $O_2$[32]. The process reproducibly and stably activates npAu materials, including ingots, foils, and shells, for the selective oxidative transformation of alcohols, regardless of material preparation method. This is especially notable given that the foils and shells likely contain a significant amount of incorporated carbon.

A small amount of $CO_2$ is evolved during the activation process, signalling the removal of carbonaceous surface poisons[32]. However, after the catalyst was activated and stabilized, the selectivity of methyl formate production from methanol was 100% on all three materials, with the foils and shells having a higher activity per unit mass (0.091 and 0.083 mmol $s^{-1}$ $g^{-1}$, respectively) than the ingots (0.017 mmol $s^{-1}$ $g^{-1}$) [32]. This indicates that the foils and shells overcome the mass transport limitations that are characteristic of the ingots. Following the initial stabilization period of approximately 12-24 hours, the catalyst materials exhibited stable methyl formate production over a month on stream. In addition, once activated, the npAu catalysts could be removed from the reactor and stored in air for a period of at least four months and, upon reintroduction to reaction conditions, they regained their activity without a second ozone treatment.

These ozone-treated npAu materials are a functionally different catalyst than the npAu activated only under flowing reactants. Ozone-activated npAu possesses high selectivity for methyl formate production, as with previous npAu catalysts, but it is active at 423 K and inactive under previously studied temperatures (< 353 K) [6,32]. Unlike reactant-activated materials, ozone-treated npAu is stably active for the selective self-coupling of both ethanol and 1-butanol to form ethyl acetate and butyl butyrate, respectively [7,32]. These self-coupling reactions with higher alcohols will be discussed in greater detail in the subsequent section. Interestingly, ozone-treated npAu also does not catalyse the oxidation of CO to $CO_2$, which is beneficial in maintaining selectivity in the presence of CO, and alludes to a fundamental difference in the activity of the oxygen on the surface of the material activated using this method. Importantly, in both types of npAu (ozone-treated and non-ozone treated), the O on the surface was provided by $O_2$, not ozone, as ozone was purged from the reactor after ozone treatment and the catalyst was allowed to stabilize prior to reactivity studies. The precise nature of the O on the surface of ozone-activated npAu is currently being studied using a method known as temporal analysis of products (TAP), which has a high sensitivity for kinetic details [40].

Differences in oxygen coverage on the npAu surface are likely to also be responsible for the variations in selectivity between methanol oxidation reactions under low-pressure conditions and at atmospheric pressure under flowing conditions. As discussed previously, in addition to methyl formate and $CO_2$, the selective oxidation of methanol on npAu under low-pressure conditions yielded formaldehyde, an intermediate in methyl formate production which was not observed as a product at atmospheric pressure [9]. In the low-pressure surface science experiment, the npAu surface was pre-covered with O prior to exposure to methanol, where in the flow reactor system, the catalyst material was subject to a continuous low concentration of both methanol and oxygen simultaneously. The sequential dosing used in the low pressure experiments may have resulted in differences in the quantity and arrangement of atomic O on the surface, thus leading to desorption of formaldehyde intact along with a significant portion of combustion to $CO_2$. However, despite some differences in selectivity between low pressure and atmospheric pressure reactions on npAu, the primary mechanism and reactivity of methanol on the surface remains the same. Further, this mechanism holds not only for methanol, the simplest alcohol, but also can be applied to predict the reactivity of longer chain alcohols such as ethanol and 1-butanol.

## 4. Applying the Mechanism to More Complex Reactants: Oxidative Self-Coupling of Ethanol and 1-Butanol

The oxidative self-coupling of longer chain alcohols, such as ethanol and 1-butanol, the vapour phase proceeds via the same reaction pathway as methanol self-coupling on both Au(111) and npAu [7,31,32,41]. As with methanol coupling, the selectivity of these reactions is critically dependent on weak interactions of reactants and intermediates with the Au or npAu surface. These interactions vary among the alcohols, and consequently, for ethanol and 1-butanol, both the esters (ethyl acetate and butyl butyrate, respectively) and the aldehydes (acetaldehyde and butyraldehyde) are produced as final products under low pressure and under atmospheric conditions [7,32,41]. This differs from methanol oxidation, where formaldehyde is not observed under catalytic conditions, but rather is only formed at low pressure conditions [9].

On the O-covered Au(111) model system these differences in selectivity are attributed to differences in the ease of β-H elimination for surface-bound alkoxides of different chain lengths [19,42]. An increase in the rate of β-H elimination with increasing chain length results in a corresponding increase in the selectivity to aldehyde production [19,42]. With the more rapid formation of the aldehyde, there are fewer alkoxides remaining on the surface for the aldehyde to react with, and thus a greater percentage of the aldehyde desorbs without reacting further.

Surface science experiments on npAu confirmed that, as predicted, these same principles also govern selectivity on the more complex npAu alloy material [31]. On npAu, evolution of aldehyde, water, and residual alcohol at the same temperature during temperature programmed experiments indicates that, as with Au(111), β-H elimination is the rate limiting step in the self-coupling of the longer chain alcohols. Interestingly, on npAu, hydrogen is also generated as a product, raising the possibility that Ag plays an additional role. However, pure Ag surfaces do not self-couple higher alcohols. Further, on npAu, the temperature for C-H bond breaking during β-H elimination is higher than on Au(111) or on an AgAu alloy surface, suggesting that the surface sites on npAu that activate alkoxy species contain Ag.

The coverage of adsorbed O also affects selectivity in the self-coupling of higher alcohols, because O on the surface assists in β-H elimination [36,38,39]. Therefore, selectivity to the self-coupled esters is greatest at low oxygen coverage, while a higher O coverage shifts selectivity toward production of aldehydes. This dependence of selectivity on O coverage is stronger for Au(111), while there is only a weak dependence on O for npAu [31,41,42]. On both Au(111) and npAu under low-pressure conditions, other secondary oxidation products, such as acetic acid and ketene for ethanol oxidation, as well as $CO_2$, are also observed at high O coverages [31,41,42]. All of these secondary combustion products result from the same rate limiting step, via an acetate intermediate [41]. Compared to the oxidative self-coupling of methanol, there is much less combustion in the selective oxidative transformations of higher alcohols [42]. Indeed, on npAu under atmospheric pressure conditions, no combustion is observed in the oxidative reactions of higher alcohols [7,32]. The decreased combustion is likely a result of the lower oxygen coverage remaining on the Au(111) or npAu surface after exposure to higher alcohols, due to the stronger affinity of the longer chain alkoxides for the surface [42].

Based on the above surface science experiments, npAu was predicted to catalyse the self-coupling of both ethanol and 1-butanol under atmospheric pressure conditions to yield the respective esters: ethyl acetate and butyl butyrate. Indeed, both ozone-treated and reactant-activated (not ozone-treated) npAu materials catalyse the selective oxidative coupling of ethanol to yield ethyl acetate [7,32]. However, the activity and consistency of selectivity are much improved on the ozone activated material [32]. The only other product in both cases was acetaldehyde—no $CO_2$ was formed. Importantly, the ozone pre-treated npAu catalysts are also stably active for the self-coupling of 1-butanol to form butyl butyrate, along with the corresponding aldehyde, butyraldehyde [ACS Catalysis]. On reactant-activated npAu, formation of butyl butyrate was not observed [7]. This is confirmation that the ozone-activation process described earlier fundamentally changes the catalytic functionality of npAu materials. In addition, the ability of npAu materials to self-couple longer chain alcohols to form esters is an indication of their Au-like catalytic behaviour, since pure Ag does not self-couple ethanol and 1-butanol, but instead produces only the aldehydes. This Au-like reactivity, in which the selectivity of partial oxidative transformations is governed by weak interactions of bound species with the surface, also defines selectivity in more complex reactant systems where two different precursor species are introduced and must compete with each other for adsorbed surface O in order to react.

## 5. Competitive Reactions Pathways: Controlling Selectivity

The key to tailoring the selectivity of coupling reactions between dissimilar alcohols on both model Au surfaces and on npAu is that selectivity is governed by the relative concentrations of the two different alkoxide species on the metal surface in addition to the relative rates of beta-C-H bond breaking in the different alkoxides [43]. Because the reactions take place on the surface, facilitated by surface O species, only alkoxides which are adsorbed on the surface can react to form aldehydes and, subsequently, esters. A hierarchy of binding strengths of different alkoxides to the Au(111) surface was developed through competition experiments using surface science techniques, including vibrational spectroscopy [43]. Two dissimilar alcohols were dosed onto a O/Au(111) single crystal, and the relative amounts of intermediates originating from each alcohol were determined via temperature programmed techniques. The relative concentrations of the intermediates were then used to predict the selectivity of the cross-coupled ester, formed from two dissimilar alkoxides, compared to either of the two self-coupled esters, which are derived from alkoxides formed from the same alcohol. For example, the binding of 1-butoxy to the surface vs. methoxy has an equilibrium constant of 10, so formation of the self-coupled ester for 1-butanol (butyl butyrate) dominates, and the optimum selectivity to the cross-coupled ester methyl butyrate is obtained with 90% methanol in the reactant mixture.

These competition studies determined that, in general, the surface stabilities of different oxygenate intermediates increase with the gas-phase acidities (Equation 1) of their precursor molecules, similar to previous studies on Ag(110) surfaces [43-45]. Because the bond cleavage of H from its conjugate base (B) is endothermic, smaller enthalpy values correspond to higher gas phase acidities. In contrast, the binding strengths of the various alkoxides do not correlate with homolytic bond dissociation energies. Importantly, there are a few outlier molecules whose relative surface stabilities are not accurately predicted using gas-phase acidities. Such molecules include fluorinated oxygenates and the relative stabilities of formate and acetate. However, these outliers can be reconciled with the predictive principles above by including the effects of weak van der Waals interactions between the molecules and the Au surface.

Theoretical studies provide strong evidence that the hierarachy of competition for binding to the surface is strongly affected by van der Waal's interactions [43]. Since the molecules all bind to the surface through a similar linkage, the relatively weak van der Waals interactions are the primary difference among the various species. The overall weak binding of intermediates to the Au surface allows these van der Waals interactions to influence binding strength in a significant way. Van der Waals interactions also affect the structure of bound species and are a prime example of the vital role that weak interactions play in determining selectivity on Au surfaces. These calculations also provide a basis for understanding the correlation between gas phase acidity and the binding to the surface. Gas phase acidity and the strength of van der Waal's interactions both correlate with the polarizability of the alkyl group. The decrease in binding to the Au surface for the $CF_3CH_2O$ is attributed to repulsion between the electron rich $CF_3$ group and the gold surface. These studies suggest that weak (van der Waal's) interactions are important in determining bonding and selectivity for longer alcohols on gold. Further, they demonstrate the importance of including such interactions more broadly in heterogeneous catalysis.

This fundamental knowledge of the stabilities of different intermediates on the surface and the surface populations of different alkoxides relative to the composition of precursor species in the reactant mixture was subsequently used to understand and predict the selectivity of cross-coupling reactions between dissimilar alcohols on the Au(111) and npAu surfaces. A simplified way to explore this system is to study the reactions between methanol and aldehydes, both on Au(111) model surfaces and on npAu. Introducing aldehyde moieties directly bypasses the $\beta$-H elimination step for the longer chain alcohol, eliminating one level of complexity. In surface science experiments, dosing of methanol to form methoxy followed by the introduction of aldehydes, such as formaldehyde, acetaldehyde, or benzaldehyde, led predominately to the formation of the cross-coupled esters formed from reaction between a methoxy and an aldehyde [46].

The strong preference of the system for cross-coupling over methanol self-coupling can be understood though studies of reaction kinetics [46]. Nucleophilic attack of the aldehydes by methoxy is kinetically favoured over $\beta$-H elimination, due to a combination of the high mobility of aldehydes on the Au(111) surface and the slow kinetics of the $\beta$-H elimination step, which is rate-limiting in the self-coupling reaction. In addition, in temperature programmed experiments, the cross-coupling between the alcohol, here methanol, and an aldehyde occurs at a lower temperature than the corresponding self-coupling reaction of either species. This is further evidence that the presence of pre-formed aldehyde increases the rate of the oxidative coupling reaction by bypassing the slow $\beta$-H elimination step. Further, as in the case of self-coupling with higher alcohols discussed previously, the presence of excess aldehyde limits the production of secondary oxidation species, such as $CO_2$. Sufficient aldehyde is available to react with methoxy to form the ester in high yield, and reaction of the aldehyde with methoxy dominates over attack of the aldehyde by adsorbed O.

Selectivity for methanol-aldehyde coupling on O-covered npAu under low pressure conditions reflects that on O/Au(111). For the cross-coupling of methanol and acetaldehyde, methyl acetate is the primary product (46% selectivity), with some methyl formate production (10%), along with combustion [47]. With butyraldehyde as the aldehyde, the cross-coupled ester, methyl butyrate, is the exclusive selective oxidation product (no methyl formate) but more $CO_2$ is produced than with acetaldehyde. Butyraldehyde adsorbs strongly to the surface, displacing adsorbed methoxy, and the lower amount of methoxy present on the surface results in cross-coupling along with secondary oxidation of residual surface-bound aldehyde.

Analogously to Au(111) and npAu at low pressure, on npAu under catalytic conditions the cross-coupled esters are dominant in the reaction between methanol and aldehydes [6,47]. As in the case of self-coupled longer chain alcohols, no $CO_2$ is observed under atmospheric pressure conditions due to the excess of aldehydes. For the reaction of methanol with either acetaldehyde or butyraldehyde, the methyl ester is the dominant product, and methyl formate becomes significant only at extreme conditions, such as when the percentage of methanol in the reactant stream is above 90-95%. The reaction rate of cross-coupling in both cases is only weakly dependent on the concentrations of methanol and $O_2$ in the reactant stream. However, the rate does increase with increasing aldehyde concentration since the reaction rate for alcohol-aldehyde coupling is not limited by a $\beta$-H elimination step. The rate of the cross-coupling reaction between methanol and either aldehyde increases with temperature, but methyl formate production also increases concomitantly because the higher temperature facilitates β-H elimination of the adsorbed methoxy species to yield formaldehyde, allowing self-coupling to take place.

As described above, the behaviour of npAu under low-pressure conditions and at atmospheric pressure is generally in close agreement with model studies on Au(111). The activation energy for methanol-butyraldehyde coupling is lower than for methanol coupling with acetaldehyde on npAu under both low-pressure and atmospheric reaction conditions [47]. This agrees with the kinetics of reactions on Au(111), where methoxy coupling with acetaldehyde is faster than coupling with formaldehyde [46]. The selectivity of npAu under low-pressure and atmospheric conditions does differ slightly, likely because of differences in surface coverages of O and reaction intermediates. In surface science experiments, dioxygen is dosed before the alcohols or aldehydes are introduced, and therefore O is able to rearrange and form locally dense patches, even if the overall O coverage on the surface is low [47]. In contrast, for the flow reactor system, there is a low steady state coverage of O because $O_2$ has a low dissociation probability on npAu, and methanol and aldehydes simultaneously compete for adsorbed O on the surface. These differences in O coverage may be responsible for the production of $CO_2$ and carboxylic acids on npAu under low-pressure conditions and their absence at atmospheric pressure.

These investigations demonstrate that the selectivity under catalytic conditions is also affected by van der Waal's interactions since the reaction selectivity as a function of the composition of the reactant mixture are observed. The correspondence in the selectivity patterns indicate that the same principles of competitive binding and weak interactions that govern selectivity in the coupling of dissimilar alcohols and aldehydes on the working npAu catalyst and on Au(111). [43]. The major difference between these two systems is that the self-coupled esters of longer chain alcohols now become possible products of the reaction with O on the surface due to the presence of both alkoxide species, rather than methoxy and an aldehyde. Therefore, the relative activation energies for β-H elimination in different alkoxides also play a role in determining selectivity between self-coupled and cross-coupled esters [19]. The activation energies for β-H elimination in alcohols decrease as follows: methoxy> ethoxy> butoxy, and thus butoxy will undergo β-H elimination more rapidly. As a result, if there are equal coverages of a higher alcohol and methanol on the surface, formation of methyl acetate or methyl butyrate will be favoured over methyl formate.

The combined effect of surface displacement and rate of β-H elimination determines selectivity on both O/Au(111) and O/npAu. Optimum selectivity for methanol-ethanol cross-coupling on Au(111) was achieved at a methanol: ethanol ratio of 85:15, with methyl acetate making up 75% of the ester yield [19]. Methyl formate accounts for 10% of the ester yield and ethyl acetate, the self-coupling product of ethanol, is 15%. The significantly higher percentage of methanol than ethanol is required in the reactants because ethanol displaces methanol on the surface. No ethyl formate was observed and methyl formate is only produced with an excess of methanol because ethanol undergoes β-H elimination to form its corresponding aldehyde at a lower temperature than methanol does. Selectivity for methanol-butanol coupling is highest at a methanol/1-butanol ratio of 90:10. Again, the cross-coupled product, here methyl butyrate, represents 75% of ester production, but the ratio of methanol to 1-butanol required is higher because 1-butanol easily displaces methanol. However, less methyl formate is produced (5% of esters), the yield of butyl butyrate is higher (20% of esters), and no butyl formate is produced because of the relative ease of β-H elimination for 1-butanol [19]. For both methanol-ethanol and methanol-butanol cross-coupling, a small amount of $CO_2$ is formed. At high 1-butanol mole fractions there is a small yield of butyraldehyde as a product, but no acetaldehyde is detected from methanol-ethanol cross coupling.

As with alcohol-aldehyde cross-coupling, selectivity on O/Au(111) is predictive of trends in selectivity on O/npAu at low pressure. At an 85:15 ratio of methanol to ethanol, methyl acetate makes up 59% of the ester yield, ethyl acetate 32%, and methyl formate 9% [48]. Esters account for 90% of the overall yield, with $CO_2$ as the residual product, and a possible trace of acetaldehyde. An important difference from Au(111) is that the ester products evolve on npAu at a higher temperature than on Au(111) [19,48]. This higher temperature is similar to the desorption temperature of these products from Ag(110), and suggests that Ag-like sites are involved in a rate limiting step of the cross-coupling transformation. For an 85:15 methanol: butanol mixture, the dominant product is the same as on Au(111), though the relative amounts of self-coupling products are different. Methyl butyrate represents 71% of the esters produced, methyl formate is 25%, and butyl butrate is 4% [48]. The decreased production of butyl butyrate is likely due to the increased yield of butyraldehyde and $CO_2$: 24% and 49% of the overall yield, respectively. The overall selectivity to esters is 28%. Studies of changes in selectivity to the different ester products over a range of alcohols ratios for methanol-ethanol and methanol-butanol coupling reveal trends in selectivity that are nearly identical to those on Au(111).

Remarkably, the trends in selectivity over different alcohol ratios are not only the same between Au(111) and npAu under low-pressure conditions, they also match the activity of ozone-treated npAu materials under catalytic conditions [48]. This correspondence is possible because the alcohols are only activated on the surface when adsorbed O is present, which prevents the accumulation of spectator species at atmospheric pressure. As with other selective oxidative transformations of longer chain alcohols under atmospheric conditions, no $CO_2$, organic acids, or formaldehyde are observed. There is also no formation of ethyl formate or butyl formate. However, acetaldehyde is generated under catalytic conditions, while it is not observed at low pressure [19,48]. At higher methanol mole fractions, ester production predominates, as was observed in surface science experiments. Above 90% methanol, there is a sharp increase in methanol self-coupling to yield methyl formate [48]. At low methanol mole fractions, selectivity shifts toward aldehyde formation. The concentration of $O_2$ has little effect on selectivity, indicating that the oxygen binding sites on npAu are saturated at low percentages of $O_2$ in the reactant stream (~3 vol. %).

The principles in the above sections not only hold for gas-phase reactions of alcohols, they also are relevant to other molecules, such as amines [49,50], and other reaction systems, such as solution-phase reactions. For instance, these principles explain why methyl esters were also the dominant product in solution-phase reactions involving oxidative coupling of alcohols over Au nanoparticle catalysts [51]. Other examples of the role of fundamental studies in predicting the reactivity of complex systems to guide the design of more active, selective, and sustainable catalysts are discussed below.

## 6. Predictive Trends in Reactivity: Extending the Principles to Other Systems

As with the example of npAu described above, surface science studies on model systems are valuable tools for determining the basic mechanistic and kinetic parameters of reactions on metal surfaces so as to fully understand and predict reactivity and selectivity on more complex materials under catalytic operating conditions. These fundamental studies can be used to understand existing catalytic systems to better optimize catalysts and reaction conditions in order to achieve greater selectivity and improve energy and resource efficiency. One example is the determination of a microkinetic model for the oxidation of methanol on Ag to form formaldehyde, which is a key industrial process [52]. Determination of mechanistic steps and rate constants for this conversion under well-controlled low pressure conditions yielded a model of reaction orders, selectivity, and activation barriers which is valid to 900K at atmospheric pressure and explains why the industrial conditions for this process are successful [52,53].

Fundamental studies can also be employed to predict novel catalytic reactivity on known materials and to design new materials for previously unachievable chemical transformations. For instance, the principles defined for the reaction of alcohols on Au surfaces can be generalized further to fundamental concepts of acid-base chemistry [43-45]. Adsorbed O acts as a Brønsted base to abstract a hydrogen from a species BH, generating a negatively polarized species, $B^-$. This species can then undergo β-H elimination to form an intermediate with an electron-deficient carbon. While the primary focus of the work discussed in this review was on alkoxides as the negatively polarized species and aldehydes as the positively charged intermediates, any molecule with an electron-deficient carbon should react with an alkoxide group on Au surfaces. Indeed, direct carbonylation of methanol to form dimethyl carbonate on O/Au(111) can be achieved via sequential nucleophilic attack of two methoxy species on an adsorbed CO molecule [54]. Dimethyl carbonate is used in a number of applications, including as a solvent[55] and in biodiesel production[56], and it replaces more toxic methylation reagents such as metal halides and phosgene[57]. This new synthetic route for producing dimethyl carbonate directly from methanol and CO is an important advance in sustainable chemistry because the current industrial process for generating dimethyl carbonate yields hydrochloric acid as a caustic byproduct [58].

Conversely, replacing the nucleophile in this reaction pathway also opens up a wide variety of new synthetic routes. Dimethyl amide ($N(CH_3)_2^-$) is an appropriate substitute for methoxy, because it is a strong nucleophile. In addition, it is known that adsorbed O on Au surfaces can activate N-H bonds [59]. Consistent with the general mechanism for O-assisted coupling on Au surfaces, after N-H bond activation of a reactant amine by the O/ Au(111) surface, the adsorbed amide moiety attacks the electron-deficient carbonyl carbon in an adsorbed aldehyde, which can either be formed from β-H elimination of an alcohol or introduced directly [49,50,60]. This results in the formation of a hemiaminal intermediate, which undergoes β-H elimination to form the final amide product. For example, the coupling product of dimethylamine and methanol via this approach is dimethylformamide. Amides are highly important in the chemical industry, particularly in the production of pharmaceuticals and polymers[61] and, as with dimethyl carbonate, the existing methods for amide production rely on acids or bases, which lead to the generation of toxic byproducts.

Importantly, this work with amines also provided mechanistic elucidation of a previous report regarding the oxidative dehydrogenation of secondary amines to imines on Au powder and alumina-supported Au particles [42]. Further, this mechanism is consistent with catalytic studies of the coupling of alcohols and amines on supported Au catalysts in alcohol solution [62]. The ability to map fundamental models onto complex materials under solution-phase reaction conditions is particularly promising, because it enables the extension of these predictive mechanisms to reactions that are not suitable to gas-phase studies, such as conversions of large biomass derivatives and other high molecular weight molecules.

Outlook:
Emphasize (1) value of fundamental studies on model systems—UHV on single crystals, UHV on actual catalytic material, and DFT. (2) Importance of van der Waal's interactions on Au.

Challenges: (1) Other materials may build up other species on the surface under catalytic conditions because they are intrinsically more reactive. Therefore, conditions for catalysis need to be selected in terms of T and P so that the coverage is similar to UHV conditions, which allows for mapping mechanisms.
(2) The relative importance of van der Waals interactions may depend on the surface because the primary bonding interaction may affect the ability of the structure to adapt to modify the vdw interactions. In addition, the effect of vdW on transition states needs to be investigated. (3) microkinetic modelling needed to more quantitatively connect model studies to working catalysts.

## 7. Conclusions

Overall, we have shown that key mechanistic principles derived from fundamental experimental studies and theory can be used to predict the behaviour of materials with complex compositions and architectures under working catalytic conditions. Specifically, the necessary role of surface adsorbed oxygen, the facilitative activity of a minority component (here Ag), and the importance of the weak binding of adsorbates as determined by surface science experiments on Au(111) and AgAu alloys govern the activity of the mesoscale porous alloy, npAu, at atmospheric pressures. The deliberate tailoring of material composition and reaction conditions in accordance with these principles enables the development of highly active catalysts, selective chemical transformations, and energy-efficient reaction conditions, all of which are vital to securing a sustainable future for industrial chemical production.

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